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Electrochemical, Polarization, and Crevice Corrosion Testing of Nitinol 60, A Supplement to the ECLSS Sustaining Materials Compatibility Study

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Prepared for Marshall Space Flight Center
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EXECUTIVE SUMMARY

In a previous study, electrochemical test results are presented for six noble metals which were evaluated in test solutions representative of waste liquids processed in the Environmental Control and Life Support System (ECLSS) aboard the International Space Station (ISS). Subsequently, a seventh metal, Nitinol 60, was added for evaluation and subjected to the same test routines, data analysis, and theoretical methodologies as those utilized during the previous study. With the earlier project, the six test metals evaluated included three titanium grades, (commercially pure, 6Al-4V alloy and 6Al-4V low interstitial alloy), two nickel-chromium alloys (Inconel® 625 and Hastelloy® C276), and one high-tier stainless steel (Cronidur® 30). The titanium alloys gave the best results of all the metals, indicating superior corrosive nobility and galvanic protection properties for the three titanium metals.

For this current effort, the results have clearly shown that Nitinol 60 is also quite noble as it is very corrosion resistant and galvanically compatible with the other six metals from both an electrochemical perspective and long-term crevice corrosion scenario. This was clearly demonstrated utilizing the same techniques for linear, Tafel and cyclic polarization, and galvanic coupling of the metal candidate as was done for the previous study. The high nobility and low corrosion susceptibility for Nitinol 60 appear to be intermediate to the nickel/chromium alloys and the titanium metals with indications that are more reflective of the titanium metals in terms of general corrosion and pitting behavior.

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CONTRACTOR REPORT

ELECTROCHEMICAL, POLARIZATION, AND CREVICE CORROSION TESTING OF NITINOL 60, A SUPPLEMENT TO THE ECLSS SUSTAINING MATERIALS COMPATIBILITY STUDY

1.0 Introduction

1.1 Background

The particular analytical methodologies and theoretical approaches employed for this current study are identical to those developed during the initial metals compatibility study evaluating Commercially Pure Titanium, Titanium 6Al-4V alloy, Titanium 6Al-4V Low Interstitial alloy, Inconel® 625, Hastelloy® C276 Cronidur® 30. These concepts and techniques were covered comprehensively in the final reports for that study. Thus, the reader is referred to two principal resources for background regarding the techniques utilized for the Nitinol 60 project.

- (1) “ECLSS Sustaining Metal Materials Compatibility Final Report, Electrochemical and Crevice Corrosion Test Results”, R.E. Lee, NASA/CR—2015–218208, April 2015, Contract NNM12AA41C
- (2) “ECLSS Sustaining Metal Materials Compatibility Final Briefing, Electrochemical and Crevice Corrosion Test Results”, October 6, 2014, Randy Lee

In accordance with the initial study, the purpose for evaluating Nitinol 60 was to evaluate potential corrosive effects and possible galvanic incapacabilities between Nitinol 60, the subject test solutions and the other metals under consideration. While the initial project call for evaluations in the alternate pretreated urine and its concentrated brine, in addition, the Nitinol study also included the baseline pretreated urine and its associated brine solution, making a total of four test solutions:

- (1) the proposed or alternate pretreated waste solution
- (2) the alternate brine concentrate derived from solution (1)
- (3) the former or baseline pretreated waste solution
- (4) the baseline brine concentrate derived from solution (3)

Since solutions (3) and (4) were not included in the test plan for the original six metals, some of the data points for the galvanic coupling phase involving these six metals were unavailable for this study. The former baseline pretreat formulation includes chromic acid and sulfuric acid while the proposed formula is based on chromic acid and phosphoric acid. Specifically, the change was from sulfuric to phosphoric

in response to issues related to precipitation effects in some of the system filters. Composition of the Nitinol 60 evaluated was 59.5% Nickel, 40.4% Titanium and 0.07% other elements. Nitinol alloys are not present in most published Galvanic Series, but they are expected to rank up near Titanium.

1.2 Polarization Concepts

Whenever the potential (voltage) and electric current (amperage) are measured and evaluated together, the potential is an indication of the nobility with respect to the tendency, probability or susceptibility for corrosion to occur. The current is directly proportional to the rate of oxidation, a quantity which can be converted into units indicating how fast the base metal is recessing *and* how fast the oxide thickness is changing. Base metal recession (etching) and oxide growth (passivation) are mutually inclusive processes. A high breakdown potential infers high nobility with low susceptibility to corrosion, while a large pitting current indicates a high pitting rate. A low corrosion potential implies a high susceptibility to corrosion while a high repassivation current demonstrates a robust oxide-restoration process (repassivation) that is characteristic of strong corrosion protection mechanisms.

2.0 Experimental

2.1 Test Sample Preparation

2.1.1 Machining and Finishing of Test Samples

All test samples were machined from bulk metal stock into approximately 3' X 3" X 1/2" plates. This size was deemed appropriate for all of the polarization, galvanic and crevice corrosion testing as mandated by the ECLSS project to satisfy the requirements for evaluating the performance and compatibility of each metal candidate of interest. All the metal samples were degreased, rinsed and dried, and then liberally rinsed with DI water, solvent rinsed and air dried in ambient atmosphere (68-72°F and 30-40% R.H.) to promote natural development of their native surface oxide layers prior to testing.

2.1.2 Crevice Sample Assembly Configuration

Samples for evaluating crevice corrosion effects were assembled in two different configurations loosely based on ASTM G78 as described below. However, the specific test approach utilized throughout these studies was developed in-house at Marshall Space Flight Center several years back.

Angled Crevice Sample Configuration

Sandwich-type assemblies consisted of two sample plates clamped together and separated by a small rectangular-shaped, single layer of filter paper near one side of the clamped assembly to create a tiny *angled crevice gap* between the two plates.

Parallel Crevice Sample Configuration

Sandwich-type assemblies consisted of two sample plates clamped together and separated by a larger square-shaped, single layer of filter paper centered in the assembly to create a tiny *parallel crevice gap* around the edges between the two plates.

2.2 Procedures and Techniques

2.2.1 Crevice Corrosion Evaluations

Test assemblies of Nitinol 60 were placed in storage in both the pretreat and brine solutions in two separate groups, one group to be evaluated after 6 months storage in each solution and another group to be evaluated after 12 months storage. Test articles consisted of two plates clamped together as ‘sandwich’-type assemblies with a single piece of filter in between the plates. After removal from the test solutions and thorough rinsing, each sample was subjected to visual and microscopic evaluation to check for signs of corrosion, surface growth, pitting, base metal degradation and/or any anomaly of relevance.

Wedge/sandwich assemblies of Nitinol 60 plates were segregated into separate storage bins, each bin containing one of the four tests solutions. Samples were monitored periodically. After six months, half of the samples were removed, carefully cleaned and evaluated. After 12 months, the remaining samples were then removed, carefully cleaned and evaluated. Since the number of plates received for the project was short by two, one of the 6-month assemblies had to be omitted. This sample was chosen to be from the baseline brine test group. However, all 12 month samples were available and evaluated so the loss in information due to the missing sample is considered to be trivial for this study.

2.2.2 Polarization Workstations and Equipment

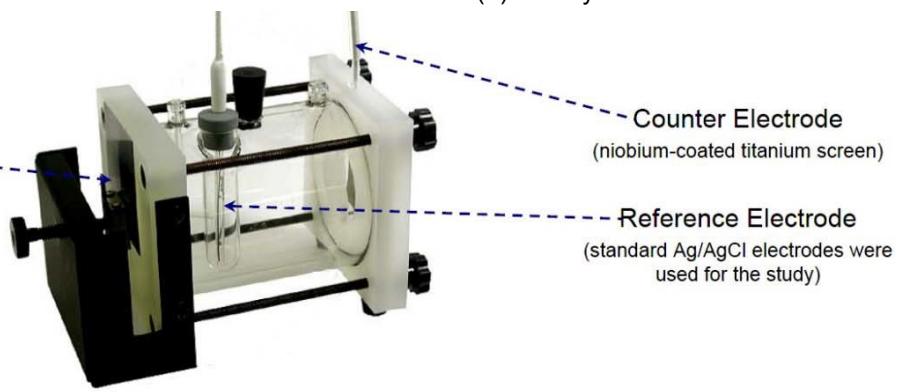
Electrochemical measurements were carried out utilizing computer-controlled potentiostat workstations supplied by Princeton Applied Research (PAR) and Gamry Instruments. Specifically, four PAR models 2273 and 273A systems along with two Gamry model 3000s were utilized throughout the study. Both of these systems included their own proprietary software for data collection and analysis. Test solutions and metal samples were accommodated using Flat Test Cells throughout the project which included 1 cm² exposure holes on one end for polarization routines and 1 cm² exposure holes on both ends for galvanic coupling. Ag/AgCl reference electrodes were used throughout. The equipment, experimental configurations and workstations are depicted in Figures 1 and 2.



(a) Parstat 2273



(b) Gamry 3000



(c) Flat Test Cell

Figure 1: Images of the (a) PAR 2273 potentiostat test system, (b) Gamry 3000 potentiostat test unit and (c) flat test cell which can be attached to either system.

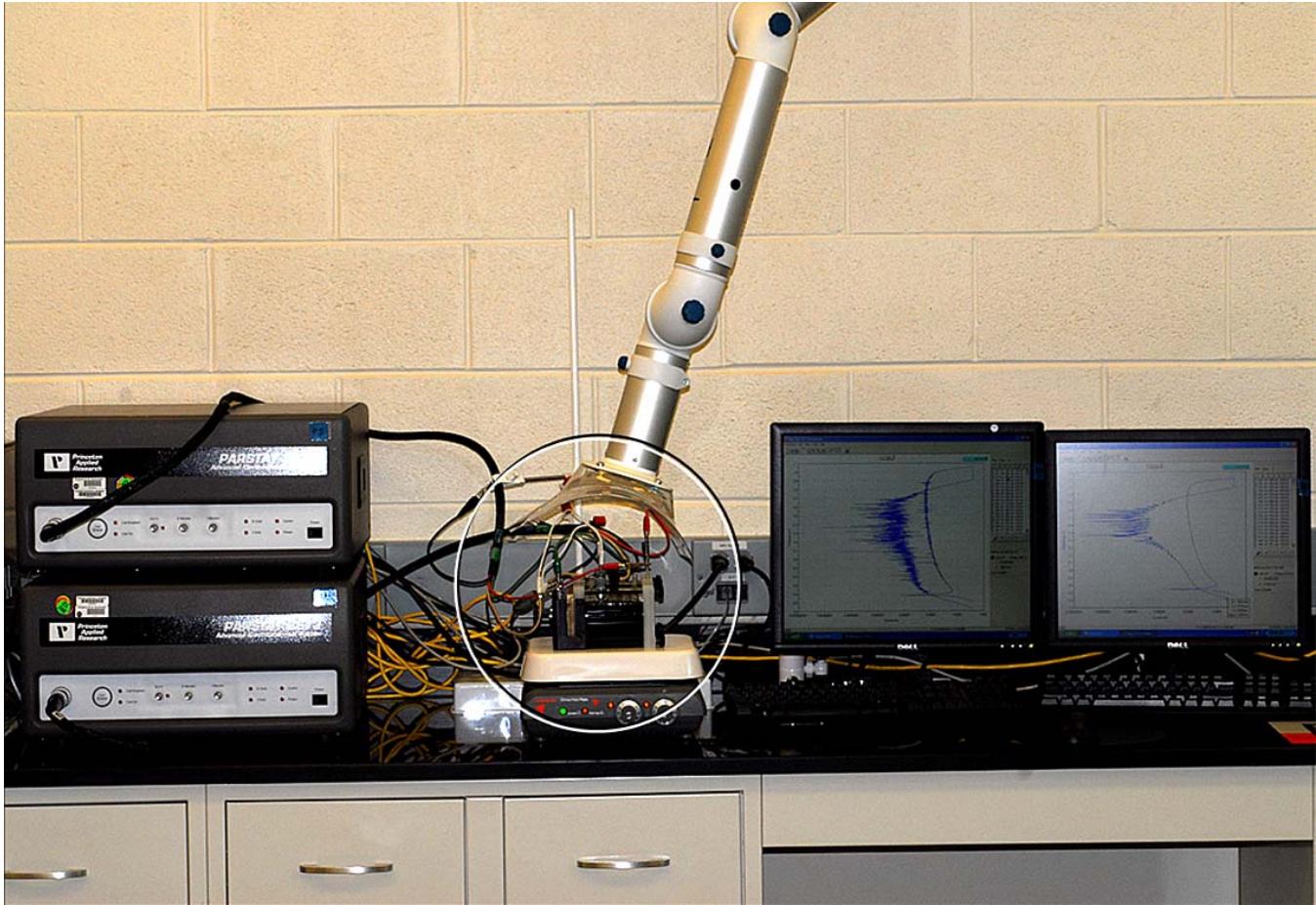


Figure 2: Typical workstation and test cell configuration showing two stacked PAR workstations with two test cells in operation (center).

The flat cell offers flexibility for a variety of DC electrochemical studies including Open Circuit, Linear, Tafel, Cyclic polarization and Galvanic Coupling measurements. For Galvanic Coupling tests, the cell is re-assembled using a second 1cm^2 sample area end-cap for the other metal so that both samples are connected across the test solution. The second metal is grounded and interacts with the first metal which is monitored for voltage and current changes.

2.2.3 DC Polarization Test Descriptions

Brief definitions of the test modules employed for this study are given below.

Open Circuit Analysis (OCP) – Measures the steady state potential (voltage) E_{oc} as a single metal is exposed to the solution over time with no power applied. This portion of the test can take sometimes several days to reach stabilization or steady state (constant oxidation rate) for the metals under study.

Linear Polarization – Measures the resulting current response when a very small voltage is applied (± 10 - 20 mV) relative to the OCP. This test is considered to be nondestructive. Provides the corrosion resistance R_{Cor} and the corrosion rate k_{Cor} in the preselected potential range.

Tafel Polarization – Measures current response across a larger potential range (± 200 - 250 mV) relative to the OCP. Spans the near cathodic and anodic regions close to E_{OC} providing the corrosion potential E_{Cor} , corrosion current I_{Cor} , the beta Tafel parameters and k_{Cor} . May or may not be slightly destructive.

Cyclic Polarization – Applies a broad potential cycle across the anodic passivation range, beyond the breakdown potential E_{Brk} after which the scan direction is reversed at a preselected potential E_{Ver} , called the vertex, where the potential begins to decrease, passing through the repassivation branch and back down to zero. The current is monitored throughout. A hysteresis loop is usually generated. This technique provides rates for pitting corrosion, passivation and repassivation as well as unique information regarding tendencies, susceptibilities and capabilities associated with corrosion and passivation behavior. Supplemental general corrosion information may also be obtained from cyclic polarization data.

Note: For clarity, it should be realized that the crystal structures comprising the passive oxides on these metals are not always damaged catastrophically at E_{Brk} , but rather their electrical insulator properties undergo a rapid transformation as resistance drops off and conduction increases across the layer allowing external corrosive agents to interact directly with the metal surface, possibly leading to pit initiation. This is due to the rapid increase in the mobility of charge carriers near E_{Brk} . As the voltage is further increased, tunneling of the electrons may occur and then at some point beyond E_{Brk} , the oxide structures may physically fail and start dissolving in the test solution.

Galvanic Coupling – Measures the steady state potential (voltage) E_{OCG} and current I_g as two metals interact (galvanically) across the test solution with no power applied. This test can sometimes take several days to reach a stabilized steady state for the particular metals under study.

For many researchers, their polarization test strategy includes cathodically conditioning the sample prior to or at the beginning of the test run by starting the scan at a very low potential relative to the pre-measured open circuit potential (OCP). Such treatments are intended to chemically reduce, dissolve and remove or strip the air-formed native oxide layer from the metal surface while it is immersed within the test solution under cathodically protective conditions. This induces formation of a new passive layer on the test surface as the potential passes into the anodic portion of the scan well below the original OCP. The intent is to conduct the test on an uncontaminated, freshly formed passive layer within the specific electrolytic solution of interest. The newly-formed oxide layer is very similar to the air-formed coating . . . but it is not necessarily the same.

In contrast, one of the objectives of these studies was to evaluate the metals in their natural states after immersion into the subject test solutions because this approach better represents the actual field conditions that exist when components are assembled, incorporated into the full-scale ECLSS system and exposed to pretreated and brine solutions. In any event, the oxide layer will adapt to the new environment over time. It is also realized that cathodic conditioning is not applied to the components prior to or during their normal operation environments, so such treatments were not considered to be relevant for this project. Alternatively, our test samples included final rinsing steps in DI water and solvent followed by 24 hours of ambient air drying under controlled conditions (68°-72°F, 30-40% R.H.) in order to encourage a robust natural passive layer to form on the surfaces prior to testing. However, a few complementary test samples were intentionally subjected to negative cathodic voltages during cyclic testing as part of the overall evaluation in order to better understand the effects of extreme polarization applications.

2.2.4 Polarization Test Sequence

Metal candidates were subjected to the test sequence depicted in Figure 3 below. Depending on time allocations and schedule flexibility, a minimum of 4 and up to 6 separate test sample areas were evaluated for each candidate metal in order to obtain respectable averages and test the extremes.

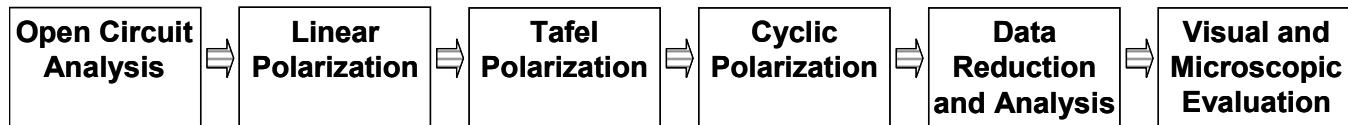


Figure 3: Incremental flow sequence for polarization testing.

2.2.5 Galvanic Coupling

In this phase of the testing, test cells are equipped with two metals, one acting as the ‘working’ electrode and the other as the ‘counter’ electrode. The test assembly is allowed to sit under open circuit conditions with no power applied while the working sample is monitored by the potentiostat for voltage and current changes as it responds to the presence of the counter sample. Increases in either potential, current or both indicate that the working metal is anodic (less noble) to the counter metal as the working metal attempts to protect itself by raising its open circuit potential (OCP) and increasing its rate of passive oxide generation. For all the metals under study, including Nitinol 60, these changes are very slight, being in the milli-volt and nano-amp ranges. If the working metal is cathodic to the counter metal, its OCP is slightly reduced while the rate of passivation decreases. Cathodic behavior indicates that the working metal is nobler than the counter metal as the working metal’s corrosion protection requirements are relaxed. This test is nondestructive. Since no power is applied to the cell, no degradation or discoloration on either of the exposed surfaces takes place, at least for the noble metals under evaluation.

3.0 Results of Corrosion Testing

3.1 Crevice Corrosion Assessment

As described previously, clamped, two-plate assemblies of Nitinol 60 were stored in each of the four test solutions for 6 months and 12 months. At 6 and 12 month intervals, designated samples were removed, carefully cleaned and visually inspected under magnification. Six month test results were presented at the Mid-Term Briefing and indicated no corrosion issues. Results of the twelve month samples were identical to the six month group with no anomalies noted on any sample surface for any of the test solutions. Group images showing one side of each angled and parallel sample surface for all four solutions are given in Figures 4 and 5. Since both interfaces in each assembly were identical, only one of the plate surfaces for each test assembly are shown for purposes of expediency.

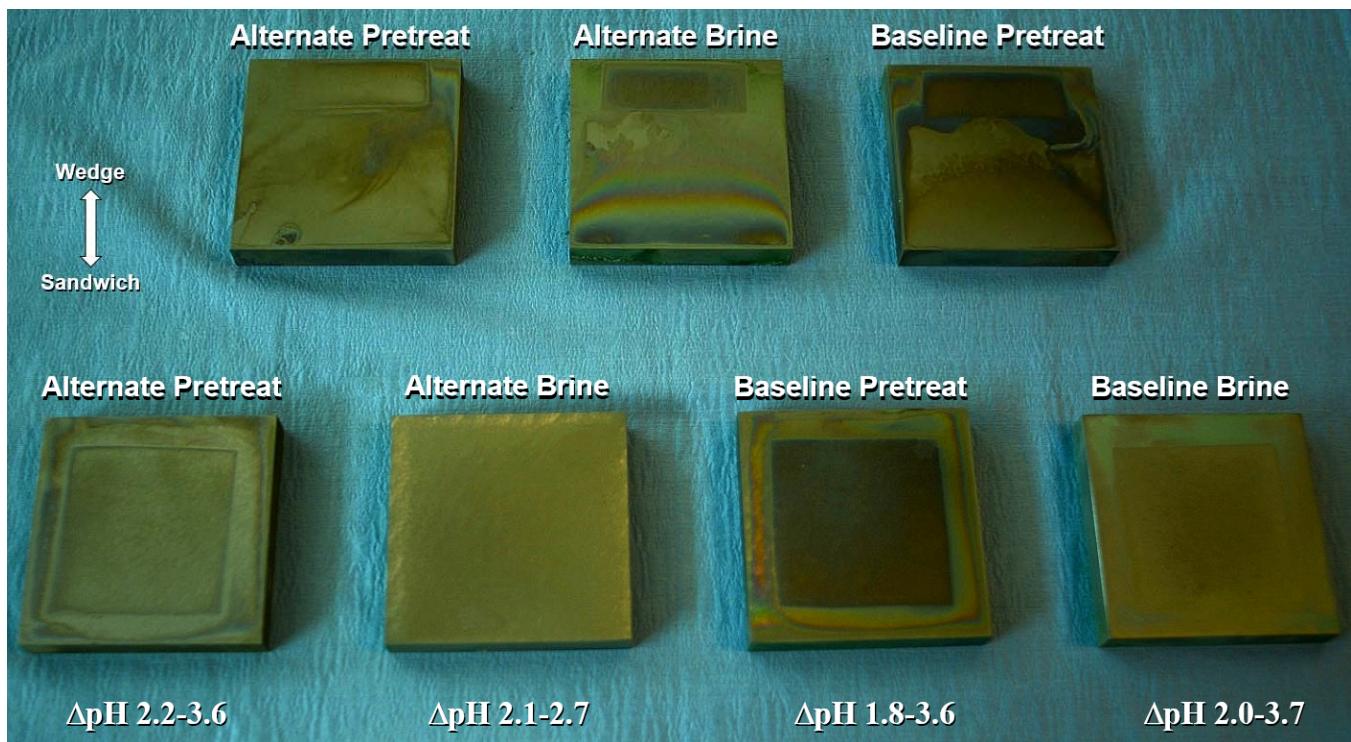


Figure 4: Images with descriptions of crevice sample surfaces after six months in the test solutions.

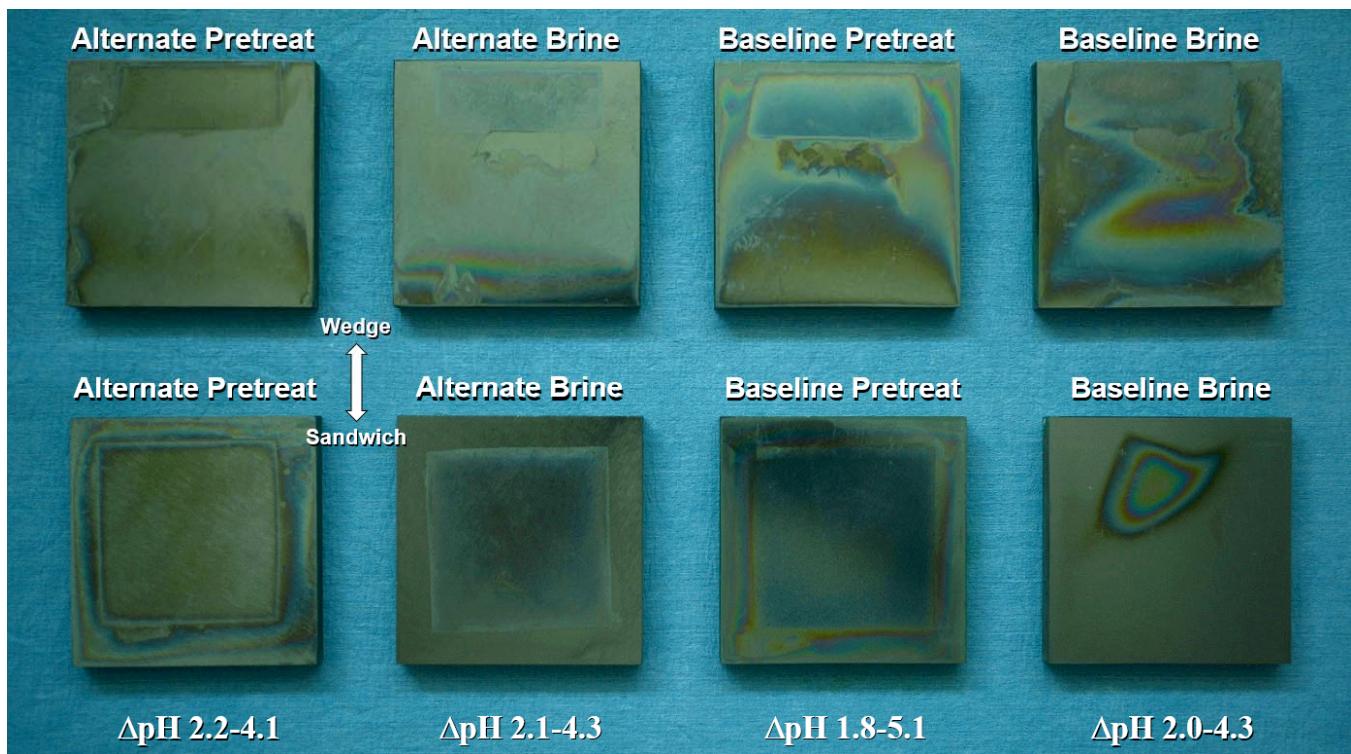


Figure 5: Images with descriptions of crevice sample surfaces after one year storage.

The pH of each storage solution was measured at the start of the test and then after the 6 and 12 month test periods. These results are provided in Figures 4 and 5. In all cases, microscopic examination indicated no visible signs of pitting, etching, recession or surface growth on any of metal surfaces for any of the test solutions. After removing the samples from the acidic test solutions, rinsing in DI water and allowing to stabilize in the ambient atmosphere, discoloration patterns were seen on some of the surfaces which were analogous to those observed on titanium samples previously. However, it has been demonstrated that these discolorations are purely superficial in nature and have no effect on the corrosion protection properties of the metal. They are believed to develop due to very slight lattice deviations in the oxide structure as it adapts to ambient conditions during the rinsing and air stabilization process.

Overall changes in solution pH indicated no anomalies which could be attributed to corrosion events since no corrosion was observed on any surface in any solution. Organism growth in and atop the alternate pretreat bath was substantial after 2-3 weeks in storage but then leveled off and remained essentially constant for the remainder of the test periods. No growth was seen in the any of the other solutions. Initial and 12-month pH values for the four test solution are given below.

- (1) Alternate Pretreat: ΔpH 2.2 – 4.1
- (2) Alternate Brine: ΔpH 2.1 – 4.3
- (3) Baseline Pretreat: ΔpH 1.8 – 5.1
- (4) Baseline Brine: ΔpH 2.0 – 4.3

Acidic solutions are generally anodic as they force metals to elevate their corrosion protection mechanisms by increasing passive oxide regeneration. Observed increases in pH during exposure to the subject test solutions are due to consumption of acidic hydrogens from the solution as a steady state condition is established between passive layer dissolution and oxide regeneration. This was covered in detail in our previous report^[1] and is re-illustrated here as a reminder in Figure 6 below.

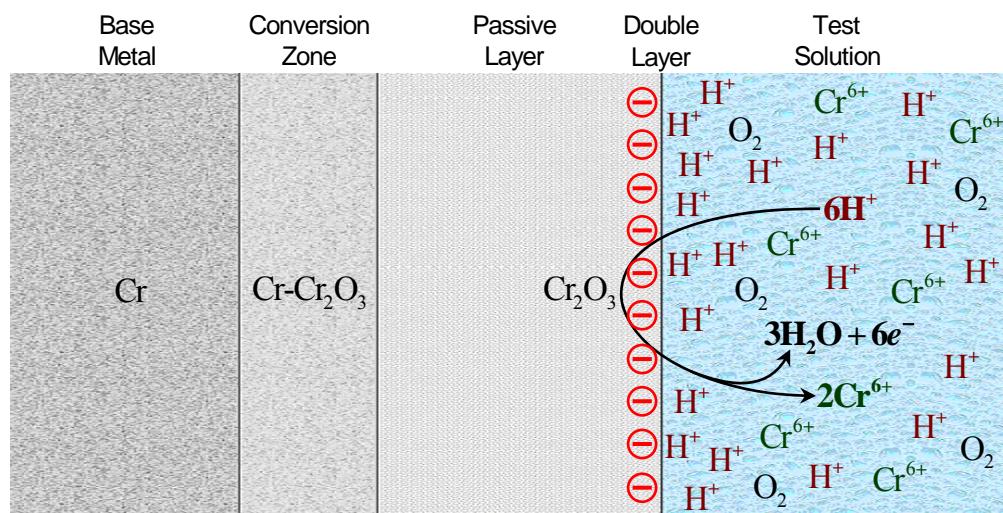


Figure 6: Illustration of a chromium-rich alloy seconds after immersion in an acidic electrolyte.

3.2 Electrochemical Assessment

In addition to evaluating the corrosion properties of Nitinol 60, part of the goal here was to better understand how Nitinol compares to the other six metals previously tested. Thus, during the final data summary process, Nitinol results were integrated into the existing data tables containing the other metals in order to provide relative indications regarding their differences in nobility and oxidation rate. On the whole, Open Circuit Potential, Linear and Tafel polarization pertain primarily to general (areal) corrosion effects while cyclic polarization provides information with respect to pitting and localized corrosion events. Reduced data summary averages and results for this test sequence are provided in Tables 1, 2 and 3. For all the tables, pretreat and brine Nitinol data is indicated in red and blue highlight respectively. Since the previous metals were not evaluated in either of the baseline solutions, this information is not available. However, baseline data for the Nitinol 60 samples is included in these tables for expediency and for relative informational purposes.

Table1: Reduced Data Summary for Open Circuit Potential Testing

Apparent Relative Nobility			Stabilization Period	
Potential Data	<u>Alternate PreTreat</u>	General Corrosion Susceptibility	<u>Alternate PreTreat</u>	~ 90% of Steady State (hours)
	Time Data		Time Data	
Titanium CP	93.9	0.36%	Titanium CP	11.8
Titanium 6-4 LI	80.8	0.39%	Titanium 6-4 LI	14.6
Nitinol 60 (Baseline)	78.2	0.49%	Titanium 6Al-4V	15.5
Titanium 6Al-4V	77.4	0.39%	Nitinol 60 (Alternate)	16.0
Cronidur 30	69.3	1.60%	Nitinol 60 (Baseline)	19.7
Nitinol 60 (Alternate)	51.2	0.50%	Inconel 625	20.6
Inconel 625	28.9	1.40%	Hastelloy C-276	27.6
Hastelloy C-276	18.7	1.51%	Cronidur 30	33.4

Alternate Brine			Alternate Brine	
Potential Data	Steady State Potential (mV _{AgCl})	General Corrosion Susceptibility	Time Data	~ 90% of Steady State (hours)
			Time Data	
Titanium CP	104.3	0.36%	Titanium CP	7.78
Titanium 6-4 LI	97.0	0.39%	Titanium 6-4 LI	13.1
Titanium 6Al-4V	95.2	0.39%	Titanium 6Al-4V	13.9
Nitinol 60 (Baseline)	84.2	0.49%	Nitinol 60 (Baseline)	14.8
Nitinol 60 (Alternate)	61.7	0.49%	Hastelloy C-276	16.6
Cronidur 30	46.5	2.41%	Nitinol 60 (Alternate)	17.7
Inconel 625	38.2	1.97%	Inconel 625	18.6
Hastelloy C-276	32.3	2.41%	Cronidur 30	24.1

Nitinol baseline solution data is included in these tables for reference only

Table 2: Reduced Data Summary for Linear and Tafel Polarization

Apparent Relative Nobility				General Corrosion/Oxidation Rates at E_{Corr}							
Alternate Pretreat				Alternate PreTreat							
Potential Data	Corrosion Potential E_{Cor} (mV _{AgCl})	Corrosion Susceptivity S_{Cor} (%)	Current Data	Polarization Resistance R_{Cor} (MΩ/cm ²)	Exchange Current I_{Cor} (nA/cm ²)	Anodic Constant β_a (mV _{AgCl})	Cathodic Constant β_c (mV _{AgCl})	Metal Recession Rate Commonly reported as Corrosion Rate (Å/day)	Oxide Growth Rate = Inward+outward growth ≡ Dissolution Rate (Å/day)	Metal Recession Rate (mil/year)	Oxide Growth Rate (mil/year)
Titanium CP	69.1	0.37%	Titanium CP	0.27	467	257	187	89.4	0.128	226	0.325
Titanium 6-4 LI	64.8	0.3958%	Titanium 6-4 LI	0.15	413	205	143	82.7	0.119	258	0.371
Titanium 6Al-4V	63.9	0.3964%	Titanium 6Al-4V	0.10	444	280	187	88.5	0.127	277	0.398
Nitinol 60 (Alt)	24.7	0.501%	Nitinol 60 (Alt)	0.12	611	325	89.9	71.9	0.103	242	0.347
Cronidur 30	17.3	1.63%	Cronidur 30	0.08	498	456	95.9	61.4	0.088	311	0.447
Inconel 625	15.7	1.41%	Inconel 625	0.09	579	461	81.2	79.2	0.114	383	0.551
Hastelloy C-276	14.0	1.51%	Hastelloy C-276	0.11	517	225	43.2	72.3	0.104	336	0.482
Nitinol 60 (Base)	11.2	0.504%	Nitinol 60 (Base)	0.09	383	298	133	77.6	0.112	261	0.375

Alternate Brine				Alternate Brine							
Potential Data	Corrosion Potential E_{Cor} (mV _{AgCl})	Corrosion Susceptivity S_{Cor} (%)	Current Data	Polarization Resistance R_{Cor} (MΩ/cm ²)	Exchange Current I_{Cor} (nA/cm ²)	Anodic Constant β_a (mV _{AgCl})	Cathodic Constant β_c (mV _{AgCl})	Metal Recession Rate Commonly reported as Corrosion Rate (Å/day)	Oxide Growth Rate = Inward+outward growth ≡ Dissolution Rate (Å/day)	Metal Recession Rate (mil/year)	Oxide Growth Rate (mil/year)
Titanium CP	80.2	0.36%	Titanium CP	0.70	388	1044	207	88.8	0.128	225	0.323
Titanium 6-4 LI	77.5	0.39%	Titanium 6-4 LI	0.29	345	254	192	69.1	0.099	215	0.310
Titanium 6Al-4V	68.4	0.40%	Titanium 6Al-4V	0.60	419	241	185	60.9	0.088	191	0.274
Nitinol 60 (Alt)	31.1	0.500%	Nitinol 60 (Alt)	0.09	557	357	116	63.3	0.091	213	0.306
Hastelloy C-276	23.1	1.51%	Hastelloy C-276	0.18	446	830	216	51.9	0.075	241	0.346
Inconel 625	22.7	1.40%	Inconel 625	0.17	317	1459	229	43.4	0.062	210	0.302
Cronidur 30	20.9	1.63%	Cronidur 30	0.34	315	746	178	38.9	0.056	197	0.283
Nitinol 60 (Base)	14.9	0.503%	Nitinol 60 (Base)	0.11	513	345	115	61.9	0.089	208	0.299

Nitinol baseline solution data is included in these tables for reference only

Table 3: Reduced Data Summary for Cyclic Polarization Testing

Potentials & Rates Associated With Pitting Corrosion & Protection					Propensities Associated With Pitting Corrosion & Protection					
Alternate PreTreat					Alternate PreTreat					
	Maximum Passivation Potential (mV _{AgCl})	Oxide Breakdown Potential (mV _{AgCl})	Maximum Repassivation Potential (mV _{AgCl})	Maximum Gross Pitting Rate (mil/year)	Maximum Repassivation Rate (mil/year)	Area of Hysteresis Loop (mV-A)	Pitting Recovery Ratio (PRR) (k_{ReP} / k_{Pit})	General Recovery Ratio (GRR) (I_{Cor1} / I_{Cor2})	Susceptibility for Pitting Initiation ($f(E_{Brk} - E_{Pas})$)	Susceptibility for Pitting Sustainment ($f(E_{Brk} - E_{ReP})$)
Titanium CP	128	2315	1904	0.18	1.31	-1.31	7.06	33.6	0.51%	0.46%
Titanium 6-4 LI	101	2287	1749	0.18	1.36	-1.52	7.56	6.29	0.64%	0.48%
Titanium 6Al-4V	116	2157	1733	0.24	1.70	-2.88	7.17	8.42	0.80%	0.49%
Nitinol 60 (Alt)	110	1447	1403	0.77	3.38	-0.93	5.80	1.42	1.00%	0.45%
Nitinol 60 (Base)	119	1144	1229	0.97	4.22	-1.88	5.31	0.69	1.34%	0.69%
Inconel 625	129	996	911	2.61	5.51	-0.33	2.17	693	5.85%	1.02%
Hastelloy C-276	146	950	809	2.22	4.27	-0.23	2.53	758	6.77%	0.49%
Cronidur 30	150	653	196	5.83	2.16	+22.6	0.47	1.33	9.18%	6.46%

Alternate Brine						Alternate Brine				
	Maximum Passivation Potential (mV _{AgCl})	Oxide Breakdown Potential (mV _{AgCl})	Maximum Repassivation Potential (mV _{AgCl})	Maximum Gross Pitting Rate (mil/year)	Maximum Repassivation Rate (mil/year)	Area of Hysteresis Loop (mV-A)	Pitting Recovery Ratio (PRR) (k_{ReP} / k_{Pit})	General Recovery Ratio (GRR) (I_{Cor1} / I_{Cor2})	Susceptibility for Pitting Initiation ($f(E_{Brk} - E_{Pas})$)	Susceptibility for Pitting Sustainment ($f(E_{Brk} - E_{ReP})$)
Titanium CP	149	2303	1729	0.33	1.74	-0.63	7.46	19.5	0.53%	0.50%
Titanium 6Al-4V	98	2302	1671	0.29	2.26	-4.59	7.30	5.43	0.63%	0.57%
Titanium 6-4 LI	118	2179	1242	0.26	1.48	-4.01	7.87	4.15	0.68%	0.60%
Nitinol 60 (Alt)	131	1712	1695	1.02	4.73	-0.69	7.97	6.96	1.03%	0.15%
Nitinol 60 (Base)	105	1391	1403	1.16	5.24	-1.05	4.92	3.97	1.10%	0.43%
Inconel 625	153	1046	858	3.37	7.99	-0.22	2.35	510	5.80%	0.27%
Hastelloy C-276	117	903	836	3.92	9.23	-0.17	2.39	697	6.87%	0.37%
Cronidur 30	141	766	261	13.3	2.69	+17.6	0.19	20.4	11.5%	4.81%

Nitinol baseline solution data is included in these tables for reference only

As defined previously^{[1],[2]}, expressions for relative Corrosion Susceptibility were developed specifically for these studies. They are structured as modified Weibull-type functions of the measured Steady State (Open Circuit) Potential and the net dielectric constant of the composite passive oxide. Methodologies for estimating base metal Recession Rate and passive Oxide Growth Rate are based on Faraday's law utilizing metal components comprising the composite oxide layer (rather than the base metal) as outlined previously^{[1],[2]}. All parameters developed for the cyclic polarization evaluation were also defined utilizing techniques covered in References (1) and (2). Potentials and gross rates are either surmised or taken directly from the data plots. In general, the Pitting Recovery Ratio (PRR) and General Recovery Ratio (GRR) both increase as the metal exhibits a higher resistance to pitting corrosion. When the vertex is reached (voltage reversal point), the metal passivation system is given the opportunity to recover or repair itself. The form of the hysteresis loop is reflective of this recovery process. Hysteresis loops become positive when the data trace continues to proceed with a forward vector after the vertex. Such behavior indicates that pitting may still be occurring during (and in spite of) the repassivation-recovery process. On the other hand, negative hysteresis infers that the repassivation forces have

overwhelmed any pitting that may have been occurring prior to the vertex. Cronidur 30 was the only metal that showed positive hysteresis while all the other metal candidates, including Nitinol 60, exhibited negative hysteresis with strong repassivation/recovery effects at work. The PRR is a contrast between the repassivation rate and the pitting rate while the GRR contrasts the Tafel corrosion rates during initial passivation and repassivation. In general, high PRR and GRR values indicate robust protection mechanisms during the recovery process after dielectric breakdown has occurred.

Overall, these results correspond very well with estimated relative pitting susceptibilities. Susceptibilities for pitting initiation and sustainment are formulated as potential difference functions centered around the dielectric breakdown potential (E_{Brk}) and utilizing potentials for initial passivation and repassivation. Again, Nitinol 60 appears to be intermediate in pitting properties relative to the nickel alloys and the titanium metals. While the nickel alloys indicate slightly higher susceptibilities for pit initiation, their protection mechanisms greatly subdue continued growth of pitting. On the other hand, Nitinol 60, like the titanium metals, shows a low susceptibility for both pit initiation and sustained growth. Under standard testing conditions, none of the previous metals showed any signs of corrosion while the titanium metals appeared to possess the best performance of all. All six metals exhibited high nobility and would be expected to rank at the top of any Galvanic Series on metals in most environments. The same can be said of Nitinol 60. In analogy to the titanium metals, the tendency for general corrosion or pitting to occur with Nitinol 60 in either of the alternate solutions is effectively nil. It is also obvious that the propensity for and rate of corrosion for Nitinol 60 in both of the baseline solutions is trivial. For reference, a typical cyclic polarization plot for one of the Nitinol samples is given in Figure 7 along with descriptions of the various regions and points of interest.

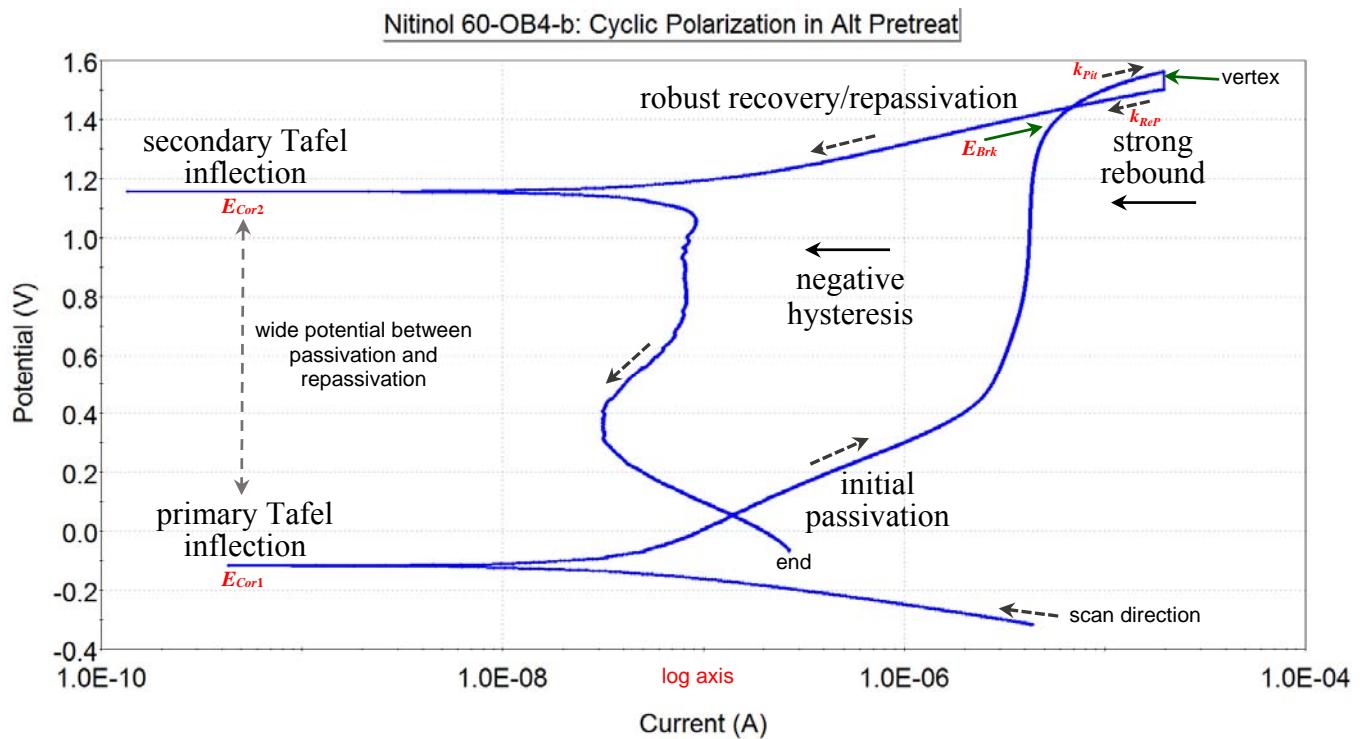


Figure 7: Data plot of Nitinol 60 cyclic polarization test run (blue trace) with descriptions.

3.3 Galvanic Coupling Assessment

In order to more completely evaluate the performance of Nitinol 60 amongst the other six metals, galvanic coupling trials were conducted in which each metal was paired up against each of the other six metals individually until coupling data was obtained for all seven metals. As described earlier, the ‘test’ metal is monitored for potential and current changes over time with no power applied as its OCP is shifted in response to the presence of the ‘counter’ metal. Since all these metals are highly noble and very close to each other electrochemically, only very small changes were expected. As indicated earlier, polarization and galvanic data in the baseline solutions were not provided for the six metals during the previous study, and quantities of the test solutions for the current study were limited. Thus, some of the baseline pretreat and brine data for the previous six metals in the two baseline solutions is not available. Nevertheless, all of the coupling information pertaining to the alternate pretreat and brine solutions and most of that pertaining to the baseline solutions was tabulated and evaluated as shown in Table 4 which gives the reduced data summary averages for all metals and solutions available at the time of this study.

Table 4: Reduced Data Summary for Galvanic Coupling Evaluation

	Galvanic Couple Current (<i>I</i>) and Potential Change Relative to OCP (ΔP)																	
	Inconel 625			Hastelloy C276			Titanium CP			Titanium 6-4			Titanium LI			Cronidur 30		
	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift	<i>I</i> nA	ΔP mV _{AgCl}	TM Shift
Alternate Pretreat																		
Nitinol as Test Metal (TM)	-38	31	-20	-12	36	-15	2	70	19	5	66	15	15	71	19	-4	11	-40
Nitinol as Counter Metal	24	45	21	14	28	10	-8	50	-44	-6	45	-32	-4	38	-43	7	65	26
Alternate Brine																		
Nitinol as Test Metal (TM)	-38	35	-26	-30	28	-34	8	78	16	3	76	14	5	87	25	-16	21	-41
Nitinol as Counter Metal	27	67	29	21	48	15	-5	54	-50	-10	62	-34	-6	29	-68	22	77	30
Baseline Pretreat																		
Nitinol as Test Metal (TM)	-46	49	-29	-18	54	-24	8	91	13	7	97	18	8	89	11	-18	33	-46
Nitinol as Counter Metal	44	87	X	31	65	X	-15	78	X	-12	24	X	-6	51	X	29	-128	X
Baseline Brine																		
Nitinol as Test Metal (TM)	-45	40	-44	-6	52	-32	11	95	11	2	100	16	4	105	21	37	46	-38
Nitinol as Counter Metal	-33	54	X	25	40	X	-21	44	X	-10	32	X	-9		X	56	67	X

Paragraph 2.2.5 gives an excellent guideline for helping to understand these results and is reiterated here for convenience. Each galvanic test cell is equipped with two metals, one acting as the Test Metal (TM) and the other as the Counter Metal. The test assembly is allowed to sit under open circuit conditions at the test temperature of $100^{\circ}\pm 5^{\circ}\text{F}$ with no power applied while the Test Metal is monitored by the potentiostat for small voltage and current changes as it responds to the presence of the Counter Metal. Increases in either potential, current or both indicate that the working metal is anodic (less noble) to the counter metal as the working metal attempts to protect itself by raising its open circuit potential (OCP) and increasing its rate of passive oxide generation. If the Test Metal is cathodic to the Counter Metal, its

OCP is slightly reduced while the rate of passivation decreases. Cathodic behavior indicates that the working metal is nobler than the counter metal as the working metal's corrosion protection requirements are relaxed. Potential changes are indicated by the TM Shift in Table 4. Thus, negative currents and/or negative TM Shifts infer that the Test Metal is cathodic (more noble) than the counter metal it is paired up with, while positive currents and/or TM Shifts indicate that the Test Metal is anodic (less noble) than the counter metal it is paired up with. Collectively, for all seven metals evaluated, potential and current shifts are quite small, being in the milli-volt and nano-amp ranges. As a matter of fact, these changes are so minute that galvanic differences between the seven metals are completely irrelevant. They are well within the 250mV limit provided in Table 2 of NASA-STD-6012^[3].

Due to the close proximity of these seven metals in terms of nobility and the fact that no power is applied, this test is completely nondestructive, producing no surface degradation of any kind. Again, the nobility placement of Nitinol 60 appears to somewhere be in between the nickel/chromium and iron/chromium alloys (625, C276 and 30) and the three titanium metals. It is perhaps a little closer to the titanium metals. Therefore, it is concluded that Nitinol 60 is compatible with the six metals tested previously for both the alternate pretreat and alternate brine solutions. One could probably make a strong argument that all seven metals are also compatible in both of the baseline solutions as well.

3.4 Summary of Electrochemical Testing

- **General Corrosion:** All Nitinol 60 samples exhibited insignificant general corrosion rates and very pronounced surface oxide recovery/repassivation protection mechanisms in all four test solutions as indicated by Linear, Tafel and Cyclic polarization test results.

The corrosion-resistant behavior of Nitinol 60 was reflective of the Titanium alloys evaluated previously. Specifically, results indicated that the nobility and metal recession rates for Nitinol 60 may be better than Inconel 625 / Hastelloy C276 and almost on par with the Titanium metals.

- **Pitting Corrosion:** As demonstrated throughout the polarization testing sequence, none of the Nitinol samples indicated any signs of pitting or localized corrosion either visibly or during analysis of cyclic polarization data for any of the four test solutions.

Superficial surface discolorations were apparent on some of the sample areas reminiscent of those observed on several of the Titanium sample surfaces tested previously. However, it has been concluded that these aberrations have no effect on the corrosion protective properties of the metals.

Under normal test conditions, surfaces exhibited no visible degradation after cyclic polarization. For informational purposes, a couple of samples were subjected to damaging anodic potentials in order to evaluate the extremes. These developed a very slight, thin layer of white precipitate (likely $TiO_2/Ti(OH)_4$) and one exhibited minor recession (etching) into the base metal. To a lesser degree, these effects are analogous to those exhibited previously on some of the high nickel alloys.

- **Galvanic Coupling:** No anomalies were noted through this phase of the testing as all exposed sample surfaces looked identical to the surfaces prior to testing. Potential and current changes have demonstrated that Nitinol 60 is galvanically compatible with Inconel 625, Hastelloy C276, Titanium CP, Titanium 64, Titanium LI and Cronidur 30 in all four test solutions.

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1. “ECLSS Sustaining Metal Materials Compatibility Final Report, Electrochemical and Crevice Corrosion Test Results”, R.E. Lee, NASA/CR—2015–218208, April 2015, Contract NNM12AA41C
2. “ECLSS Sustaining Metal Materials Compatibility Final Briefing, Electrochemical and Crevice Corrosion Test Results”, October 6, 2014, Randy Lee
3. “Corrosion Protection for Space Flight Hardware”, NASA Technical Standard NASA-STD-6012, March 8, 2012

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14. ABSTRACT In earlier trials, electrochemical test results were presented for six noble metals evaluated in test solutions representative of waste liquids processed in the Environmental Control and Life Support System (ECLSS) aboard the International Space Station (ISS). Subsequently, a seventh metal, Nitinol 60, was added for evaluation and subjected to the same test routines, data analysis, and theoretical methodologies. The previous six test metals included three titanium grades, (commercially pure, 6Al-4V alloy and 6Al-4V low interstitial alloy), two nickel-chromium alloys (Inconel® 625 and Hastelloy® C276), and one high-tier stainless steel (Cronidur® 30). The three titanium alloys gave the best results of all the metals, indicating superior corrosive nobility and galvanic protection properties. For this current effort, the results have clearly shown that Nitinol 60 is almost as noble as titanium, being very corrosion-resistant and galvanically compatible with the other six metals electrochemically and during long-term exposure.					
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